Journal of Alloys and Compounds 704 (2017) 390–397

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Raman study of coupled electronic and phononic excitations in LuB_{12}

Yu. S. Ponosov [a, b, *], A.A. Makhnev [a], S.V. Streltsov [a, b], V.B. Filipov [c], N. Yu. Shitsevalova [c]

[a] M.N. Mikheev Institute of Metal Physics UB RAS, 620990, S. Kovalevskaya Str. 18, Ekaterinburg, Russia
[b] Ural Federal University, Mira St. 19, 620002, Ekaterinburg, Russia
[c] I. N. Frantsevich Institute for Problems of Materials Science of National Academy of Sciences of Ukraine, 3 Krzhizhanovskogo Street, 03680, Kiev, Ukraine

ARTICLE INFO

Article history:
Received 13 August 2016
Received in revised form
23 January 2017
Accepted 29 January 2017
Available online 31 January 2017

Keywords:
Inelastic light scattering
Electron-phonon interactions
Anharmonicity
Rare earth alloys and compounds

ABSTRACT

Electronic Raman scattering and optical phonon self-energies are studied on single crystals of LuB_{12} with different isotopic composition in the temperature region 10–650 K and at pressures up to 10 GPa. The shape and energy position of the spectral peaks depend on the magnitude of the probed wave vector, temperature, and symmetry of excitations. We simulated experimental spectra using electronic structure obtained in the density functional theory and taking into account the electron-phonon scattering. The emergence of a broad continuum in the spectra is identified with the inelastic scattering of light from the electronic intraband excitations. Their coupling to non-fully symmetric phonon modes is the source of both the Fano interference and temperature-dependent phonon self-energies. In addition, long wavelength vibrations of the boron atoms are in nonadiabatic regime, so the electronic contribution to their self-energies provides a temperature dependence that is similar to the anharmonic contribution. Comparison of calculation and experiment allowed us to determine the coupling constant $\lambda = 0.32$, which gives correct critical temperature of the transition to the superconducting state.

1. Introduction

A number of superconducting substances belong to different families of binary boron compounds. Among them a record superconducting transition temperature was found in MgB_2 (T_c=39 K) [1], hexaboride YB_6 has $T_c \leq 8.4$ K [3] and dodecaboride ZrB_{12} − 6 K [2]. All of them are discussed in the framework of the conventional electron-phonon mechanism of superconductivity. The leading interaction in MgB_2 assumes strong coupling of the E_{2g} optical phonon (boron atoms vibration) with electrons. High values of the electron-phonon coupling constant λ and T_c in YB_6 and ZrB_{12} are considered to be caused by acoustic vibrations of loosely-coupled metal atoms in boron cage [4–7]. For YB_6 it is confirmed by calculations of the electron and phonon spectra, and electron-phonon interaction by linear response method [8]. However, a detailed comparison of calculation and experiment has not yet been done because of the lack of neutron data on the frequencies and widths of the acoustic phonons. Such calculations have not been performed yet for ZrB_{12} .

LuB_{12} is a structural analogue of ZrB_{12} with a considerably lower T_c = 0.42 [9]. Both crystallize in the UB_{12} structure (space group Fm-3m), where the metal atom is located in the center of a truncated boron octahedron B_{24}. Their electronic densities of states at the Fermi level are comparable. Analysis of the data on heat capacity, thermal expansion, resistivity [5] and optical spectroscopy [6,7] suggests that abovementioned difference in the T_c is due to a stronger coupling of acoustic phonons (vibrations of the zirconium atoms) with electrons in ZrB_{12}.

Contribution of high-frequency vibrations of the boron atoms to electron-phonon coupling has been studied theoretically for YB_6 [8]. It has been shown that it is small, but the comparison of calculation and experiment is missing. The phonon spectra in the region of high frequencies at normal conditions in different dodecaborides were demonstrated to be similar [10–14], but temperature and pressure effects on the dynamics and electron-phonon interaction have not been studied yet. Partly this gap can be bridged by a study of their influence on Raman active phonons. Asymmetry of the phonon lines observed in a number of borides clearly indicates their interaction with the electronic continuum. Electronic excitations are indeed observed in inelastic light scattering of hexaborides LaB_6 and YB_6 [15,16]. Their detailed study allowed us to obtain information about the velocity of electrons and their relaxation rate which is closely related with the magnitude of the electron-phonon coupling. If the difference in T_c between ZrB_{12}

* Corresponding author. M.N. Mikheev Institute of Metal Physics UB RAS, 620990, S. Kovalevskaya Str. 18, Ekaterinburg, Russia.
E-mail address: ponosov@imp.uran.ru (Yu.S. Ponosov).

http://dx.doi.org/10.1016/j.jallcom.2017.01.319
0925-8388/

and LuB_{12} is indeed due to interaction with low-frequency phonons the latter compound may serve as a reference object for study of electron-induced effects on optical vibrations.

The aim of our work is to study the effect of electron-phonon interaction on optical phonons in LuB_{12}. For this we performed measurements of the frequencies and widths of optical phonons as well as the spectra of electronic excitations in the wide range of temperatures (10–650) and pressures (0–10 GPA). Calculation of the phonon self energies and spectra of electronic excitations was performed on the basis of density functional theory (DFT). Account of the carrier scattering by phonons allowed to reproduce the anomalous temperature behavior of the self-energy of the E and T phonons, which is partly determined by the nonadiabatic interaction with the intraband electronic continuum.

2. Experiment

The single-crystal samples LuB_{12} were grown by vertical crucible-free inductive floating zone melting in an inert gas atmosphere in IPM NASU (Kiev). The details are presented in Ref. [17]. Measurements were carried out on samples with natural isotopic composition and samples enriched with isotopes ^{10}B and ^{11}B. For measurements under pressure thin nonoriented fragments of crystals with sizes $\sim 100\times 100\times 10$ μm were loaded into a gasketed diamond anvil cell (DAC) using a 4: 1 methanol-ethanol mixture as a pressure medium. The pressure in the cell was controlled using the ruby luminescence method. For temperature measurements single crystal samples with surface orientation (001) were placed into the optical microcryostat. The spectra were excited by 532 nm (2.33 eV) and 785 nm (1.55 eV) lines of solid-state lasers and 633 nm (1.96 eV) of He-Ne laser with power up to 5 mW, focused to a spot on the sample with a diameter of $\simeq$ 5–10 microns. To exclude surface effects, the measurements were carried out on freshly cleaved surfaces. The scattered light was detected by a Renishaw RM 1000 microspectrometer equipped with filters to exclude low-frequency Rayleigh scattering with a threshold of $\approx$ 50 cm^{-1} and a thermoelectrically cooled CCD-based detection system. The spectral resolution was ~ 2–3 cm^{-1}. A complete set of polarization geometries was used to extract Raman active phonon representations of A_{1g}, E_g and T_{2g}; XX (A_{1g}+E_g), XY - T_{2g}, X′Y′ - 3/4E_g, where X,Y ∥ [100], [010], and X′,Y′ ∥ [110], [$\bar{1}$10].

For the calculation of the distribution of wave-vector transfers, ellipsometric measurements of the optical constants n and k were performed. Since the optical properties of LuB_{12} in the visible spectral range vary significantly, the spectra were corrected for the optical absorption, transmission and refraction, as well as the spectral response of the spectrometer. All figures below show Raman response $\chi''(\omega)$ obtained after correction by $n_B(\omega,T)+1$, where $n_B(\omega,T)$ is the Bose-Einstein factor.

3. Raman results and calculations

3.1. Electronic response

Fig. 1 shows LuB_{12} spectra measured in different polarization geometries at T = 300 K on a single crystals enriched by isotopes ^{11}B and ^{11}B. They contain 5 narrow lines superimposed on a broad background, which intensity depends on the scattering symmetry. The continuum is strongly polarization dependent, with large E_g+T_{2g} symmetry and negligible A_{1g} symmetry contributions. The shape and position of the observed continuum do not change in measurements on the samples with different isotopic composition while the phonon lines show shifts in consistence to atomic mass ratio. Raman response $\chi''(\omega)$ for different temperatures is shown in Fig. 2. The spectra observed with 633 nm (1.96 eV) laser excitation (Fig. 2A) are very similar to ones measured in Ref. [18]. The low-temperature continuum near 185 cm^{-1} in these spectra shifts to higher energies and broadens with increasing temperature. As one can see the intensity of the broad continua goes to zero at all temperatures when $\omega\rightarrow 0$. Significant broadening and shift of the peaks to $\simeq$ 800 cm^{-1} was found with increase in temperature to 650 K. When using 532 nm (2.33 eV) laser excitation the maximum of low-temperature continuum is observed near 300 cm^{-1} (Fig. 2b). Its energy is close to the energy of the continuum at 300 K, measured with 633 nm laser excitation. As was shown in Refs. [15,16], such scattering in borides originates from intraband electronic transitions near the Fermi level. The spectra independence from isotope composition confirms their relation with electronic excitations.

3.2. Optical phonons

The number of Raman-active phonon modes for idealized structure of the dodecaborides (space group Fm-3m) is determined by a factor group analysis:

$$\Gamma_{q=0} = A_{1g} + 2E_g + 2T_{2g}. \quad (1)$$

A_{1g}, E_g and T_{2g} are irreducible representations for O_h point group. All five phonons are vibrations of the boron sublattice only. The shape of the E_g^1 and T_{2g}^1 phonon lines at 650 and 790 cm^{-1} (Figs. 1 and 2) is a striking evidence of electronic origin of broad continua. They show a strong asymmetry depending on the excitation wavelength (Fig. 3) that suggests interference between phonon line and continuum. In this case the phonon line shape may be described by the asymmetric Breit-Wigner-Fano (BWF) profile expression [19]:

$$I(\omega) = \pi\rho(\omega)T_e^2\frac{(Q+\varepsilon)^2}{1+\varepsilon^2}, \quad (2)$$

$$\varepsilon = \frac{\omega-\omega_0-V^2R(\omega)}{\Gamma}, \quad (3)$$

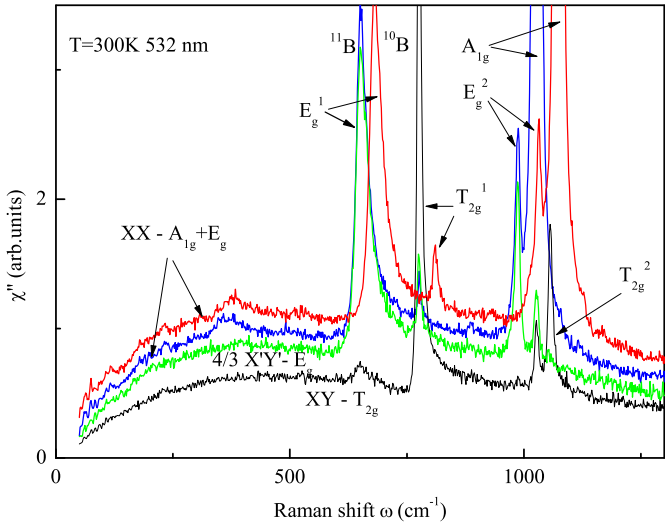

Fig. 1. Raman response $\chi''(\omega)$ in LuB_{12}, enriched by ^{10}B and ^{11}B isotopes, obtained from the (001) plane at 300 K in different polarization geometries with 532 nm excitation. Intensities of three upper spectra are almost equal and the spectra were shifted for clearness.